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Increasing the hydrothermal stability of mesoporous SiO_2 with methylchlorosilanes – a 'structural' study

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Abstract

Mesoporous silica gels with various pore sizes are hydrophobised by liquid-phase silylation with mono- and difunctional methylchlorosilanes. Changes in the pore structure as a result of the silylation reactions are monitored in order to assess the distribution of the hydrophobic groups. Extensive polymerisation of dimethyldichlorosilane (DMDCS) causes blocking of the micropore fraction. For silica with pore sizes in the supermicroporous range (2 nm pore diameter), this leads to hydrophobisation of almost exclusively the outer surface. While for trimethylchlorosilane (TMCS) a smaller number of molecules react with the surface, modification is more homogeneous and an open structure is optimally preserved. Both silanes lead to lower surface polarity and increased hydrothermal stability, i.e., preservation of the porous structure during exposure to water. As DMDCS reacts more extensively, this agent would be recommended for ceramics with pore

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diameters larger than about 6 nm. TMCS is the most suitable agent for pore diameters smaller than 4 nm and in case preservation of micropores is required.

Keywords: Mesoporous SiO_2 gel; Silylation; Hydrophilic/hydrophobic modification; Hydrothermal stability; Dimethyldichlorosilane; Trimethylchlorosilane

1. Introduction

Many applications in which adsorption processes are involved strongly rely on the use of porous silica. Typical fields include chromatography, heterogeneous catalysis and membrane technology. Characteristics that contribute to the applicability of silica include chemical inertness and high mechanical and thermal stability. As the surface is typically occupied by a large number of hydroxyl groups, enabling strong H-bonding with water, these materials are hydrophilic by nature [1,2]. Application of microporous and mesoporous materials in wet atmospheres will thus lead to rapid filling of the pores, which impairs the applicability in moist gas mixtures. Under severe conditions, water may even cause dissociation of Si-O-Si bonds, which will eventually give rise to another physical structure. In the case of membranes and chromatography, this leads to destruction of the functionality of the separation properties and limits the operating conditions under which they can be applied.

The number of hydroxyl groups can effectively be decreased by calcination at high temperature, but this process is reversible upon exposure to water. Replacement of hydroxyl groups by hydrolytically stable groups with a hydrophobic character such as CH_3 groups can inhibit the adsorption of water more effectively. One approach is to build in this organic functionality by in situ hydrolysis and condensation of alkoxide precursors with hydrophobic side groups, such as organoalkoxysilanes or bridged

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silsesquioxanes [3-5]. However, reproduction of such sol-gel derived materials involves full control over all preparation parameters and is consequently generally difficult to achieve. In addition, precursors are usually expensive and preparation is very time-consuming. Although this approach is most suitable for the synthesis of non-porous and ultramicroporous materials, for the abovementioned reasons it is solely used in small quantities for advanced applications, such as thin layers and coatings.

In case bulk quantities are required of hydrophobised ceramics with larger pores, i.e. meso- and macropores, the most obvious approach is post-modification by grafting the internal pore surface with hydrophobic groups. One of the possible hydrophobisation methods is a chemical reaction between chloride groups of an organochlorosilane with the surface hydroxyl groups. A thermally stable chemically bound layer is thus formed, which imparts the desired hydrophobicity. Successful modification has been carried out of unsupported materials for chromatography [6-9] and of composite materials such as membranes, e.g. by fluorinated silanes [10,11], chloro- and organoalkoxysilanes [12,13]. Except for hydrophobisation, a large number of post-modification procedures with various functional groups have been studied for catalyst preparation with silica as the active phase carrier, e.g. [14]. Preservation of the structure [15,16] can however also be an important additional requirement for separation applications.

High hydrophobicity can be achieved by using agents with long organic tails, as only one bond with the solid material is needed for the creation of a large hydrophobic surface. However, constraints in the application of such agents are set by the pore size of the materials due to steric hindrance. Another method that can give rise to effective surface hydrophobisation is the use of organosilanes with two or more reactive groups. As these agents may couple with two adjacent OH-groups, they may

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more effectively reduce the number of vicinal OH-groups that are responsible for the strongest hydrophilic interaction [1,2,17]. However, the functional groups may also react with each other, thereby forming a polymeric layer that has limited covalent attachment but can still be very effective in surface hydrophobisation [18,19]. A high extent of modification of γ-Al_2O_3 membranes was thus found for multifunctional methylalkoxysilanes, and included the inner surface of pores with a diameter of 5 nm [20]. The pore volume was however strongly reduced, which was explained by polymerisation reactions. Modification of mesoporous γ-Al_2O_3/TiO_2 multilayer membranes with difunctional C1 and C8 organochlorosilanes showed the highest hydrophobicity for C8 silanes [21], which supports the view that silanes with long organic tails are advantageous. For microporous membranes, it was shown that silane coupling reactions took place in pores situated at the outer membrane surface, while reactions at the internal surface were sterically hindered for both C1 and C8 silanes.

In earlier work on γ-Al_2O_3 powders [22] we demonstrated that both monofunctional ($(CH_3)_3SiCl$) and a difunctional ($(CH_3)_2SiCl_2$) methylchlorosilanes can be effective for bulk modification of mesoporous materials with pore sizes around 4-5 nm. Steric hindrance limits the use of silanes with long organic tails to materials with much larger pore sizes. Similarly, (trifunctional) methyltrichlorosilane led to extensive modification of mostly the outer surface due to polymerisation reactions and is thus also unsuitable for bulk modification of materials with small mesopores. In the present paper, we study hydrophobisation of silica gel with DMDCS (dimethyldichlorosilane) and TMCS (trimethylchlorosilane). Silica materials are studied with various pore sizes in order to assess the limits of application of these two agents for hydrophobisation. To this end, the extent of grafting and the resulting hydrothermal stability are studied with respect to changes in the pore structure.

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Simply applicable liquid phase silylation with the addition of a nucleophile (water) was chosen for its high reaction rate at low temperatures [15]. Surface and pore modification were studied by N_2 and CO_2 physisorption, TPO-MS, and SEM.

2. Experimental

2.1. Materials preparation

Silica gel powders (35-70 μm, >99% SiO_2) were obtained from Grace Davison. Analytical data as provided by the supplier are given in table 1. In order to remove any adsorbed species and to obtain similar degrees of hydroxylation, all materials were first heated in air at 773 K for 5 h. Hydrophobisation was carried out by dropwise addition of silanes to 8.67 g of material in a mixture of 50 ml water and 21.6 ml of isopropanol (Aldrich, 99.9% pure), and subsequent refluxing for 30 min during continuous stirring. Prior to addition of the silane, the material was left in the liquid mixture for 5 minutes. This procedure was expected to give rise to homogeneous hydrophobisation. As the OH-group is smaller than the Cl-group, the large amount of water ensures sufficient hydrolysis of the silanes and thus minimum steric hindrance upon the reaction with the surface OH-groups. Trimethylchlorosilane ($(CH_3)_3SiCl$, TMCS, 99% purity) and dimethyldichlorosilane ($(CH_3)_2SiCl_2$, DMDCS, 99% purity) were obtained from Aldrich.

After modification, the materials were dried, washed 3 times with water/ethanol and dried in air at 393 K. In order to obtain theoretically similar silane surface densities, the used amounts depended on the silica surface area as given by the supplier. For silica S1, materials with different silane surface densities were synthesised. DMDCS-modified materials are designated as S*n*_d, and TMCS-modified materials as S*n*_t,

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with *n* the number corresponding to the original silica material and 'd' or 't' referring to the number of methyl groups in the silane.

2.2. Materials characterisation

For assessing the extent of surface modification, Thermogravimetric Analysis-Mass Spectrometry was carried out in a Setaram TG 85 thermobalance. During heating of the materials in synthetic air (20% O_2 in N_2, 99.999% purity, 60 ml/min), their weight was recorded as a function of the temperature. Initial masses were typically 150 mg. Heating took place with 10 K/min to 1073 K (held for 30 min). A correction for the temperature-dependency of the buoyancy was performed. Analysis of reaction products was carried out simultaneously by means of a quadrupole mass spectrometer. In this way, carbon-containing molecules and fragments could be identified in the off-gas, which assisted in determination of the thermal range in which oxidation of the organic moieties took place.

Adsorption/desorption isotherms of N_2 (77 K) and CO_2 (273 K) have been determined on a CE-Instruments Sorptomatic 1990. All materials were pre-treated by evacuation below 10^{-4} mbar at 473 K. Continuous corrections were being made for variations in the atmospheric pressure p_0. For S1, surface areas were determined by the Dubinin method, modified by Kaganer [23,24], from both the N_2 and CO_2 adsorption isotherms. Surface areas and *C*-values for S2 and S3 were determined by BET-3 fits from the N_2 adsorption isotherms [24,25] between p/p_0=0 and 0.5, according to:

$$n/n_m = C(p/p_0)/(1 - p/p_0) \times (1 - (N+1)(p/p_0)^N + N(p/p_0)^{N+1}) / (1 + (C-1)(p/p_0) - C(p/p_0)^{N+1}) \quad (1)$$

with *n* the gas adsorbed at relative pressure p/p_0, n_m the monolayer capacity of the surface, both in mol per g adsorbent, *C* a constant related to heat of adsorption and

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thus to the adsorbate-adsorbent interaction and *N* the number of adsorbed layers. The area occupied by a N_2 molecule in the completed monolayer was taken to be 0.162 nm^2 (ISO 9277) and by CO_2 0.179 nm^2. Mesopore size distributions and mean mesopore diameters were obtained from BJH fits of the N_2 desorption isotherms [26] between p/p_0=0.35 and 0.9. Zero contact angle between silica surface and N_2 liquid has been assumed in the Kelvin equation used in BJH analysis. Values for the thickness of the *t*-layer were used with a dependency on the interaction between adsorbate and adsorbent (i.e. on *C*) as determined by Lecloux [27]. Cylindrical pores have been assumed for all materials as this enables good comparison of the different samples. While trends can thus be well observed, it should be noted that the exact pore diameters may be slightly different due to uncertainties in the pore geometry [16, 28]. Total mean pore diameters, including micropores and assuming cylindrical pores, were obtained by the relation:

$$d_p = 4\, v_p / A \qquad (2)$$

with d_p the pore diameter, v_p the pore volume determined at p/p_0=0.95 and *A* the surface area. In order to compare the pore volumes of the different samples, the isotherms are displayed in terms of volume of adsorbed N_2 liquid, assuming a density of 0.8086 g/cm^3 for N_2.

High resolution Scanning Electron Microscopy was carried out on a LEO Gemini 1550 FEG-SEM at a voltage of 2.0 kV.

Hydrothermal stability was determined by exposing the silica materials to doubly distilled water (373 K) for 24 h. Afterwards, the materials were dried and the structure was again investigated by means of adsorption techniques and SEM, using the same pre-treatment procedures.

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3. Results

3.1. Efficiency of modification

Weight loss of the silica powders was observed by TGA-MS during heating in synthetic air. A sharp decrease around 373 K could be attributed to the desorption of water, and a weight loss over the whole range up to 1073 K to dehydroxylation. For modified silica, ignition of the carbon-containing groups took place in a narrow thermal range around 800-850 K, which became evident from MS signals that could be associated with CO_2 and other organic components. A clear peak in the differential weight superposed on the contribution of dehydroxylation could thus be separated and the corresponding CH_3 content assessed by assuming full oxidation (table 2). Thermal analysis thus assisted in determining the surface coverage with methyl groups. The efficiency of modification, i.e. the number of reacted silane molecules with respect to the total amount of silane present in the liquid, is much larger for DMDCS (an average of 34%) than for TMCS (9%). One explanation for the higher DMDCS yield may be polymerisation due to the persisting availability of fresh reactive sites. This will give rise to partially bound chains of polymerised DMDCS, which has also been indicated by Wood [18]. In contrast, if TMCS reacts with a silanol group, no additional reactive sites can be formed. Besides a species that reacted with the surface, only dimers, i.e., hexamethyldisiloxane, could be formed, which have likely all been washed out, or desorbed at lower temperatures (boiling point=374 K).

Modifications of similar materials with larger particle sizes indicated somewhat smaller yields for DMDCS, which could indicate that the outer surface is modified first.

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3.2. Structure after modification

3.2.1. Supermicroporous S1

Adsorption/desorption isotherms of N_2 and CO_2 were determined for pure silica (calcined at 773 K in air) and for silica that was modified with DMDCS and TMCS. Only a small decrease of the surface area and the total pore volume was found after calcination, implying that our pre-treatment procedure does not lead to an essentially different structure. N_2 isotherms of the unmodified and modified silica gels are shown in Figure 1a. All isotherms are of type Ib, characterising supermicroporous materials.

Modification with both DMDCS and TMCS led to smaller pore volumes (table 2). For TMCS, the extent of modification and the decreases in pore volume, N_2 and CO_2 surface areas all follow the same trend. As the filling mechanism of the pores is different for CO_2 and N_2, the absolute surface areas determined with these molecules should not be compared directly. However, changes with respect to the unmodified material can be observed nicely. The mean pore sizes remained roughly unchanged. For extensive modification with DMDCS, on the other hand (sample S1_d2), both the pore volume and surface area decreased to almost zero, which indicates that the inner pores were not any more accessible to N_2. No blocking of the pores was observed with CO_2, however, which can be explained by the higher absolute temperature. Assuming that polymerisation of DMDCS took place, a polydimethylsiloxane (PDMS)-like material will have been formed. This material has a glass-transition temperature around 150 K and is thus rigid at 77 K and quite mobile at 273 K. At the higher temperature the organic groups will be more mobile and thus allow passage of the CO_2 molecules. As no decrease of the CO_2 area was found with respect to the unmodified material, it appears that the inner pores have hardly been modified. The extremely high CH_3 surface density is also related to the dense outer

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PDMS-like layer and the corresponding low N_2 area measured. For a much smaller extent of DMDCS modification (S1_d1), such extensive pore blockage was not observed. A significant decrease of the surface area was still found, with $A(N_2)$ in the same order of magnitude as for S1_t1, but with less than half the total number of silane molecules. Based on this smaller extent of modification, a much more limited decrease in surface area $A(N_2)$ and pore volume would be expected. Moreover, a (minor) increase of the pore diameter was found with respect to the unmodified material (table 2), indicating that mostly the smallest pores have become blocked towards permeance of N_2 molecules. This is again a strong indication that the outer surface has predominantly been modified by DMDCS and is supported by the absence of a decrease in CO_2 area for S1_d1 with respect to that of unmodified silica, similar as for S1_d2.

With SEM, a hazy image is visible on the surface for the DMDCS-modified silica S1_d2 (Figure 2b). This indicates the presence of a mobile, non-conducting layer, which is typical for organic polymers. As such hazy parts were not observed for the TMCS-modified materials, the formation of a PDMS-like layer by DMDCS on mostly the outer surface of the particles is once more affirmed.

3.2.2. Mesoporous S2 and S3

Isotherms of the unmodified and modified silica gels S2 and S3 are shown in Figure 3a and 4a. All isotherms are of type IVa. The parallel adsorption and desorption branches are typical of mesoporosity with delayed adsorption but without network percolation effects during desorption [29]. The changes in surface area and total pore volume found after calcination were even smaller than for S1. After grafting with silanes, the pore volumes and surface areas are clearly smaller (table 3). A relation can be observed between the extent of modification (in CH_3/nm^2) and the decreases

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in surface area and pore volume (Figure 5) for both S2 and S3. The values for the S1 samples are also displayed in the figure. For the DMDCS-modified materials S1_d1 and S2_d, the relative decreases in pore volume were distinctly larger, indicating some additional blockage of pores.

Changes in the mean pore diameters, calculated form the pore volume and the surface area, and in the mean mesopore diameters were observed as well after modification (table 4). For S2, a larger extent of modification led to smaller mean mesopore sizes. As the relative effect on the pore size becomes smaller at larger pore sizes, these changes are less convincing for S3 than for S2. Net increases of the mean pore diameters d_p were however observed for the DMDCS-modified materials S2_d and S3_d. As the latter parameter also includes the micropores, these increases can be interpreted as selective blocking of the micropores due to an inhomogeneous distribution of the silanes on the surface. For the TMCS-modified materials, the total mean pore diameters decreased along with the mesopore sizes, indicating a more uniform distribution of the silane over the pores.

With SEM, it was observed that the structures of S2 (Figure 6a) and S3 hardly changed after modification. Due to the high resolution of the SEM, it was even possible to discern detailed structures with sizes around 4 to 6 nm for S2 (not visible at the magnification in figure 6a) and around 10-15 nm for S3, which corresponds well to the pore diameters displayed in table 4. For the modified samples, the surface had a somewhat smoother appearance (S2_d: Figure 6b) and suffered from charging, which is a strong indication of modification with organic moieties.

3.3. Hydrophobicity and surface polarity

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After modification, immersion into water was not possible for the modified S1 and S2 materials, while some wetting took place for the modified S3 materials. This indicates that most materials had indeed become hydrophobic after modification. Simple exposure to water is obviously not sufficient to determine the extent of hydrophobicity. Measurement of the 3-phase contact angle with water was also found to be unreliable for powders, as a flat surface is needed which is conceptually difficult to envisage for small particles with an irregularly shaped surface [30].

From the *C*-values determined from the BET-3 fits, a good indication of the surface polarity could be obtained for the S2 and S3 silicas. The *C*-value is generally considered a measure of the strength of the adsorbate-adsorbent interaction. As the N_2 molecule interacts quite strongly with polar surface groups (e.g. OH), high values characterise a hydrophilic surface for this material. After modification, the *C*-values were clearly smaller, which again indicates that modification was successful. Unmodified silica also gave rather low values, which can be explained by the high pre-treatment temperature of 773 K that led to a decreased concentration of surface hydroxyl groups. During modification, the material was exposed to a boiling water/alcohol mixture. Consequently, comparison with the *C*-values 149 and 156 for S2 and S3, respectively, determined after exposure to water (see section 3.4) indicates the effect of the organic groups more accurately, and this effect seems to be quite substantial. A relationship between the inverse of the *C*-value (related to the heat of adsorption) and the number of CH_3 units/nm^2 can be observed (figure 7). The effect of CH_3 groups on the *C*-value appears to be slightly weaker for the DMDCS-modified materials than for the TMCS-modified materials.

3.4. Hydrothermal stability

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After exposure to boiling water, clear changes were observed in the isotherms of the unmodified materials (figures 1b, 3b and 4b). For unmodified S1, the pore volume decreased to 0.258 cm^3/g. For S2, the pore volume decreased to a lesser extent, while the pore volume remained constant for S3. The surface areas of S1, S2 and S3 decreased to 433 m^2/g, 294 m^2/g, and 250 m^2/g, respectively. Larger mean pore sizes and mesopore sizes were observed for all unmodified materials (tables 2 and 4), which can be explained by dissolution and subsequent re-condensation of siloxane groups during exposure to water (see section 4).

For the TMCS-modified S1 materials, the surface areas $A(N_2)$ and $A(CO_2)$ and the pore volume increased after exposure to water, and also the mean pore sizes that were calculated from these values increased slightly (table 2). For S1_d1, the values of A and v_p showed a decrease, as did the mean pore diameter. It can be envisaged that the TMCS-modified materials were affected differently, as many small trimethyl patches were present. For the DMDCS-modified materials, both the grafted and ungrafted parts are likely larger, which enables a more extensive change in structure of the ungrafted parts during water exposure, similar to unmodified silica though to a lesser extent. Remarkably, non-zero surface area and porosity were found for S1_d2, although sorption equilibrium was not reached after times as long as 2 hours, which becomes visible from the absence of overlap between the desorption and adsorption branches. Transport of N_2 into and out of the pores was very slow, and consequently no reliable mean pore diameter could be calculated. Clearly, by exposure to boiling water, the layer that closed the surface almost entirely had slightly opened, so that N_2 molecules could pass, though still with difficulty. No decrease of the extent of modification was found, however, so only the distribution of the layer had changed. The CO_2 surface area had halved after the water treatment, which suggests that the structure of the particle interior had been affected quite severely. For modified S2 and S3, the values for $A(N_2)$ did not change. The pore volumes of the TMCS-

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modified materials increased slightly, while those of the DMDCS-modified materials remained more constant. The pore sizes calculated from these values hardly changed, and showed the same trend as the mesopore sizes (table 4). Slight increases were found for the TMCS-modified materials S2_t and S3_t, and an increase to only a very limited extent for S2_d. Clearly, the pore structure of the materials has become stabilised towards prolonged exposure to water at 373 K after modification by both DMDCS and TMCS.

The surface of the S1 and S2 materials after water exposure was investigated in detail with SEM. The surface had a needle-like appearance for S2 (Figure 6c), with pores that appeared more prominent and a bit dilated with respect to the original material. Moreover, more cracks could be observed than before water exposure. No change was observed for the modified materials, e.g. S2_d (Figure 6d). Most of the small particles between 50-300 nm that were originally present on the surface of S2 disappeared after exposure to water. This also happened largely for S2_t, but not for S2_d, which may be explained by more extensive modification of the outer surface for the latter sample, preventing washing away. For S1 (Figure 2c), a needle-like structure was also observed, which was mainly apparent from an increased surface roughness. This could also imply some pore dilation, although resolution was not high enough to actually observe structures of around 2 nm in great detail. A similar change was not observed after exposure of the modified S1 materials to water. For S1_d2 (Figure 2d), a blister-like surface was observed in addition to the hazy parts. This could be a sign of re-arrangement of the PDMS-chains. The modified materials also suffered from charging after water exposure, indicating that the organic groups were still abundantly present.

4. Discussion

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The unmodified materials studied in this paper all suffer from dilation of the pores and smaller pore volumes after exposure to water. The decrease of the pore volume was most prominent for supermicroporous S1, which has the smallest pore size. This may be explained by an Ostwald ripening-mechanism, whereby larger particles grow at the expense of smaller ones. This leads to smoothening of rough surfaces, with the largest effect for surfaces with a small radius of curvature, and thus to filling of micropores, which at the same time results in an increase of the mean pore diameter d_p. This effect would thus be the largest for materials with small pores. At the same time, the mechanism here leads to a partial collapse of the structure and thus to a smaller pore volume. For modified materials, only the ungrafted parts are subject to the same mechanism, while silica transport is restrained for the grafted parts. For TMCS-modification, even some swelling is found. Limited silica transport does take place, but the homogeneously distributed trimethyl groups prevent a collapse of the pore structure, possibly acting as a kind of template, in which the pore walls are kept away, or in practise even seem to be pushed away, from each other.

Modification leads to smaller surface areas and smaller pore volumes. Micropores may become blocked by modification with DMDCS. This is very prominent for S1 but to a lesser extent this is also the case for the micropores in S2 and S3, for which an increase of the mean pore diameter d_p was observed, and at the same time a decrease of the mean BJH mesopore diameter. However, using the same values for v_p and A, d_p would more follow the same trend for these materials if a more spherical pore geometry is assumed (with the relation $d_p = 3\ v_p\ /\ A$), resulting in smaller mean pore diameters. Except clogging of the smallest micropores, a change in pore geometry towards a more spherical shape for especially micropores can thus be assumed with respect to the original SiO_2. The effect per CH_3 group on the *C*-value was also a bit more moderate than for TMCS, which may be another sign of an

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inhomogeneous distribution of DMDCS. For TMCS, no evidence of micropore blocking was found, and it can be concluded that modification is more homogeneous. For all modified materials, the pore structure remained well preserved after exposure to water. The lowest surface polarity was obtained at a high extent of modification. This is most easily achieved for DMDCS, as the yields are higher.

The higher homogeneity found for modification with TMCS can be explained by its lower reactivity in combination with limited steric hindrance. Moreover, no polymerisation occurs that can give rise to pore blocking. TMCS is therefore the most suitable agent for bulk modification of materials with small pores. For mesoporous materials with larger pore sizes, DMDCS may be preferred for the simple reason that modification is more efficient. As we found earlier that the differences between DMDCS and TMCS are small at pore diameters of around 5 nm [21], DMDCS would be more favourable for pores larger than this. For pores of 6 nm diameter, we found here that DMDCS was slightly more effective. However, in case preservation of the micropores is required, TMCS may again be the preferred reagent. In a final case, it can be envisaged that modification of mostly the outer layer is a requirement, such as for three-phase bubble column catalysts with reactants either in the water phase or in a gaseous phase [31]. For such applications, modification may be optimised towards inhomogeneous grafting of the outer surface layer such as with DMDCS as this does not lead to changes in the catalytic properties of the particle interior.

5. Conclusions

Modification of SiO_2 with DMDCS was shown to be more efficient than with TMCS. A higher extent of modification and a lower surface polarity were obtained with DMDCS using similar amounts of reagent. Both silanes lead to an increased hydrothermal

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resistance, and a relation was found with the degree of surface occupation with methyl groups. TMCS leads to the most homogeneous distribution inside the material, while modification with DMDCS predominantly takes place on the outer surface, as observed most convincingly for supermicroporous silica. This can be explained by polymerisation of DMDCS, which may lead to the formation of a layer of polydimethylsiloxane (PDMS)-like material. Although this layer is quite mobile at room temperature, it may easily give rise to blocking of small pores, which becomes obvious at the low temperatures of N_2 physisorption (77 K). Thus, for materials with very small mesopores or micropores (around 2-4 nm and smaller), TMCS is the preferred reagent for hydrophobisation if a homogeneous distribution is required. In case preservation of micropores is not essential, DMDCS may be preferred for mesoporous materials in view of the higher extent of modification for this agent. Although micropore blockage and polymerisation reactions were prominent effects, we found no further indications of incomplete bulk modification with DMDCS for materials with pore diameters around 14 nm.

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Sample	Material	Pore volume (ml/g)	Surface area (m^2/g)	Pore diameter (nm)
S1	SI 1401	0.4	750	2
S2	SI 1404	0.9	540	6
S3	SI 1301	1.15	320	14.5

Table 1: Physical characteristics of silica materials as provided by the supplier.

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Sample	CH_3/nm^2 Designed	CH_3/nm^2 Actual	v_p (cm^3/g)	$A(N_2)$ (m^2/g)	$A(CO_2)$ (m^2/g)	Mean d_p (nm)	Mean d_p after water (nm)
S1	-	-	0.319	631	340	2.02	2.38
S1_t1	5.32	1.12	0.229	445	247	2.06	2.10
S1_t2	15.96	1.97	0.193	382	209	2.02	2.11
S1_d1	1.18	0.44	0.235	449	338	2.10	2.02
S1_d2	3.55	>100	0.002	<10	346	-	-

Table 2: Analytical data (CH_3 surface density with respect to $A(N_2)$, pore volume at p/p_0= 0.95, N_2 and CO_2 surface areas and mean pore diameters) of unmodified and silane-modified S1 (t=TMCS, d=DMDCS).

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Sample	CH_3/nm^2 Designed	CH_3/nm^2 Actual	v_p (cm^3/g)	$A(N_2)$ (m^2/g)	*C*-value (BET fit)
S2	-	-	0.840	472	87
S2_t	15.96	1.09	0.755	438	47
S2_d	3.55	1.79	0.658	360	37
S3	-	-	1.21	327	122
S3_t	5.32	0.46	1.17	331	107
S3_d	3.55	1.52	1.10	277	38

Table 3: Analytical data (designed and realised CH_3 surface density with respect to $A(N_2)$, pore volume at p/p_0= 0.95, N_2 surface area and *C*-value of the BET-3 fit) of unmodified and silane-modified silica S2 and S3 (t=TMCS, d=DMDCS).

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Sample	Mean d_p (nm)	BJH d_p (nm)	Mean d_p after water (nm)	BJH d_p after water (nm)
S2	7.12	6.09	11.29	10.44
S2_t	6.90	5.96	7.25	6.21
S2_d	7.37	5.90	7.42	6.00
S3	14.9	12.7	20.3	15.8
S3_t	14.2	12.9	15.4	13.1
S3_d	15.9	12.2	15.8	12.2

Table 4: Mean pore diameters (calculated from pore volume and surface area) and mean mesopore diameters (BJH method) of unmodified and silane-modified silica S2 and S3 before and after exposure to water.

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Figure captions

Figure 1: N_2 adsorption/desorption isotherms of unmodified and modified S1 (a) before and (b) after exposure to water.

Figure 2: SE micrographs of (a) S1, (b) S1_d2, (c) S1 after exposure to water and (d) S1_d2 after exposure to water. SEM voltage: 2 kV.

Figure 3: N_2 adsorption/desorption isotherms of unmodified and modified S2 (a) before and (b) after exposure to water.

Figure 4: N_2 adsorption/desorption isotherms of unmodified and modified S3 (a) before and (b) after exposure to water. The dashed curves refer to S3_d.

Figure 5: Relation between decrease in pore volume and silane surface density for various modified silica materials (S1: diamonds, S2: squares, S3: triangles; open symbols: TMCS modified, closed symbols: DMDCS modified). The trendline represents an average of all values. S1_d1 and S2_d exhibit a relatively large decrease in pore volume.

Figure 6: SE micrographs of (a) S2, (b) S2_d, (c) S2 after exposure to water and (d) S2_d after exposure to water. SEM voltage: 2 kV.

Figure 7: Measure of N_2-surface interaction from the *C*-value of the BET-3 fit of isotherms of unmodified and modified S2 and S3 versus the CH_3 surface density.

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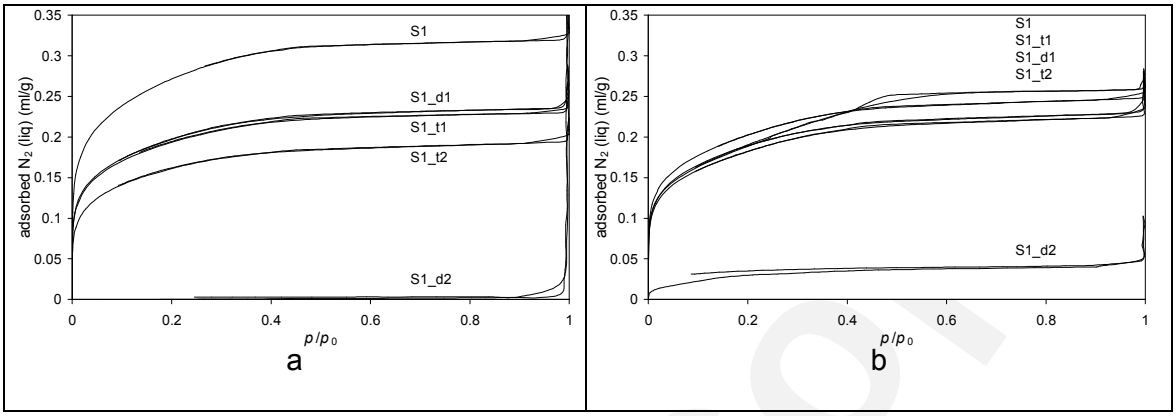
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0.25
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0.15
0.1
0.05
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adsorbed N2 (liq) (ml/g)
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S1_d1
S1_t1
S1_t2
S1_d2
0
0.2
0.4
0.6
0.8
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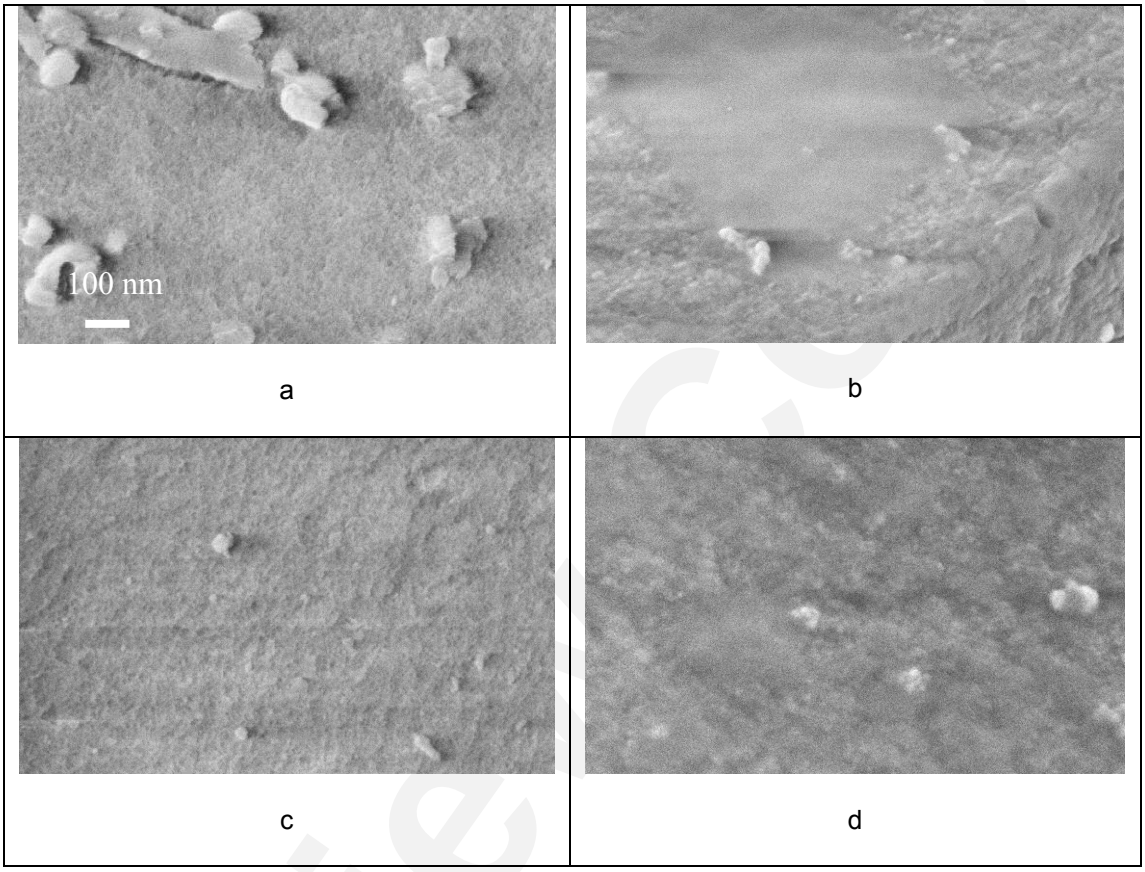
p/p0
a
S1
S1_t1
S1_d1
S1_t2
S1_d2
b

Figure 1



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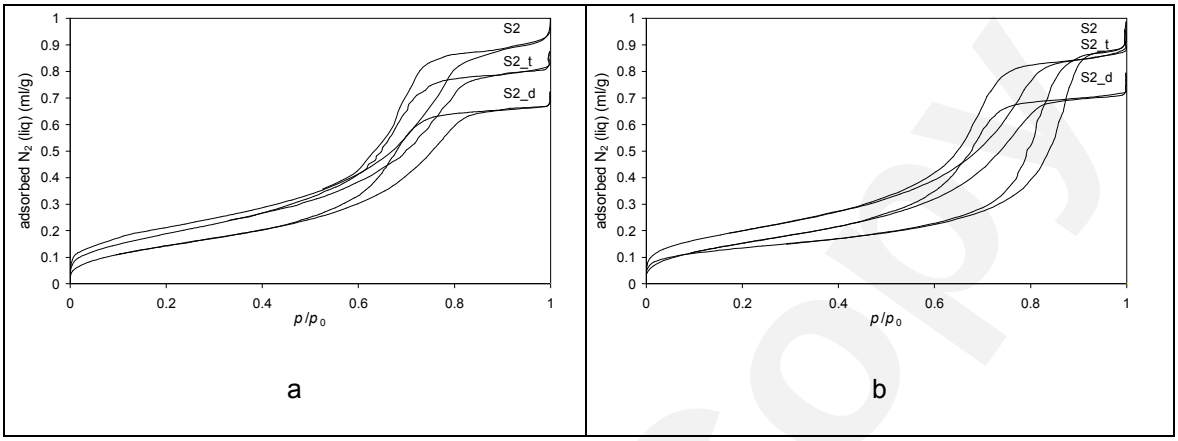

Figure 3

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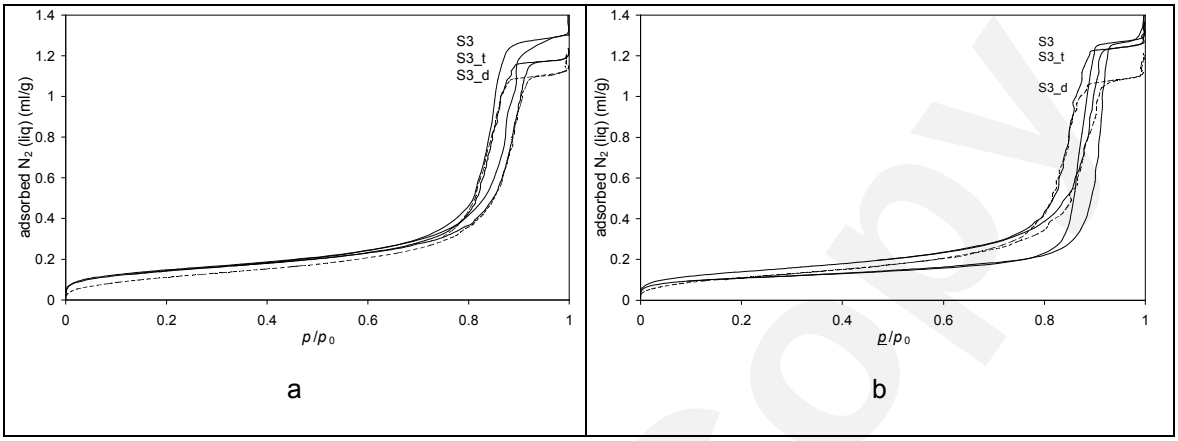

Figure 4

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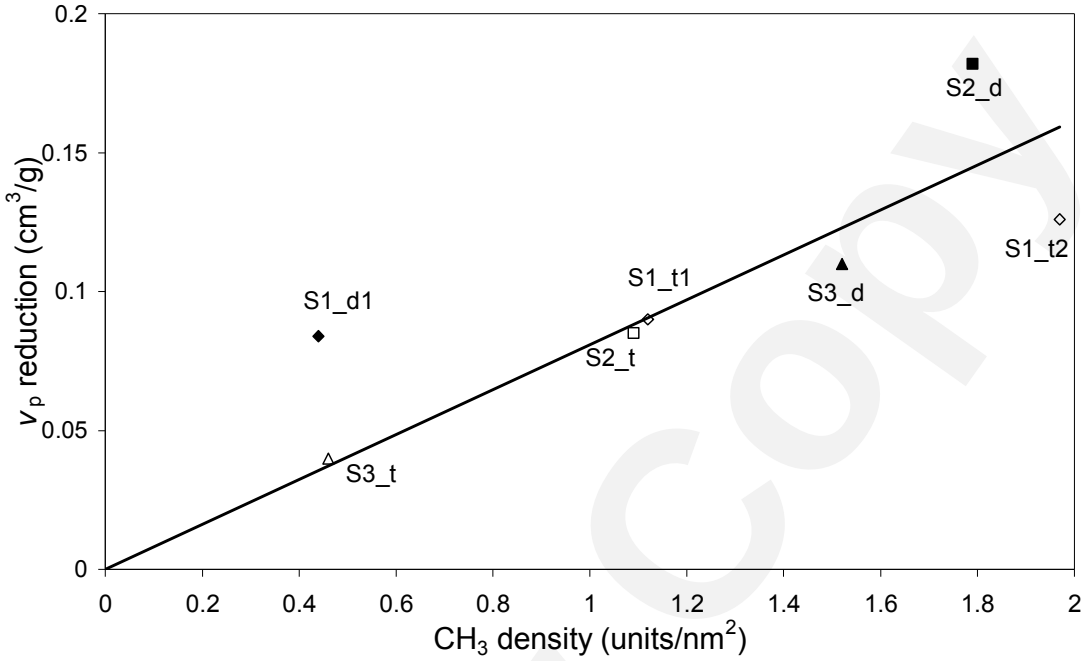

Figure 5

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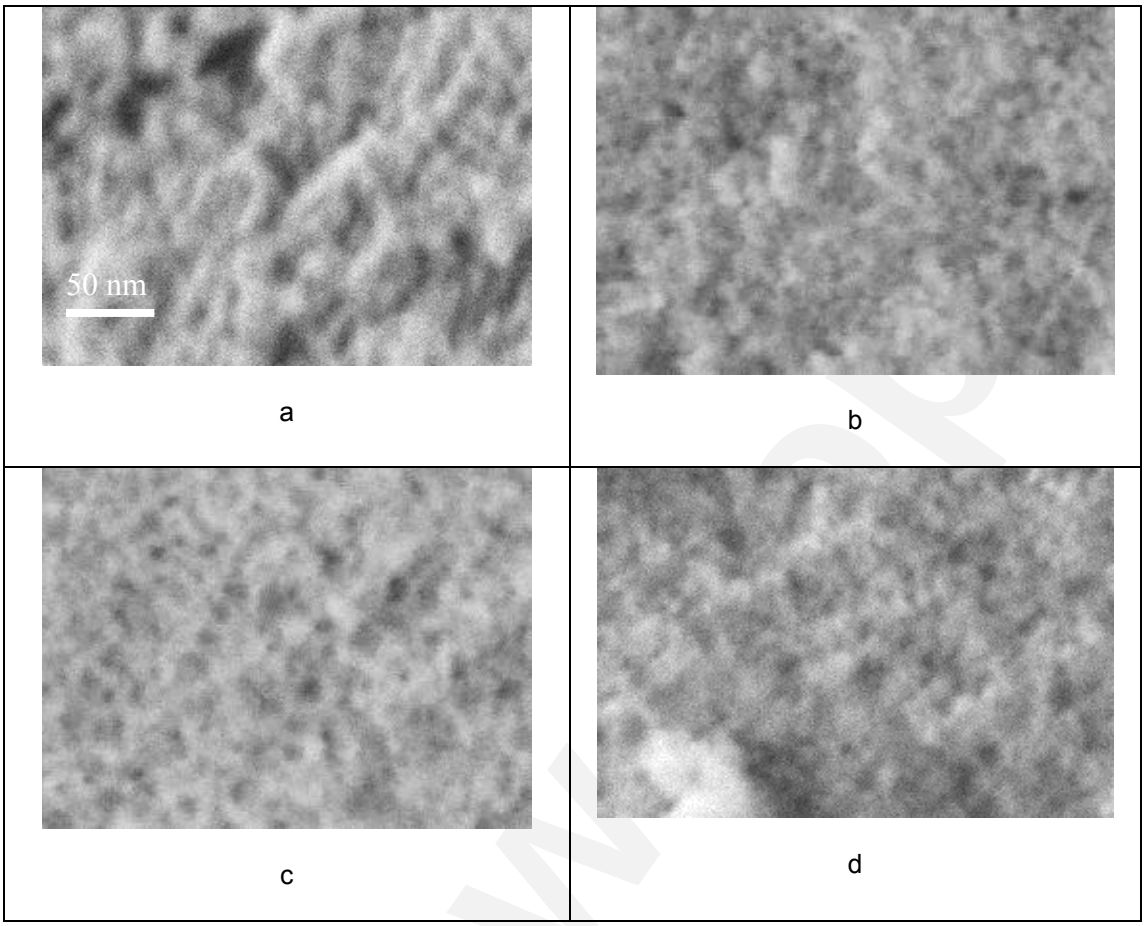

Figure 6

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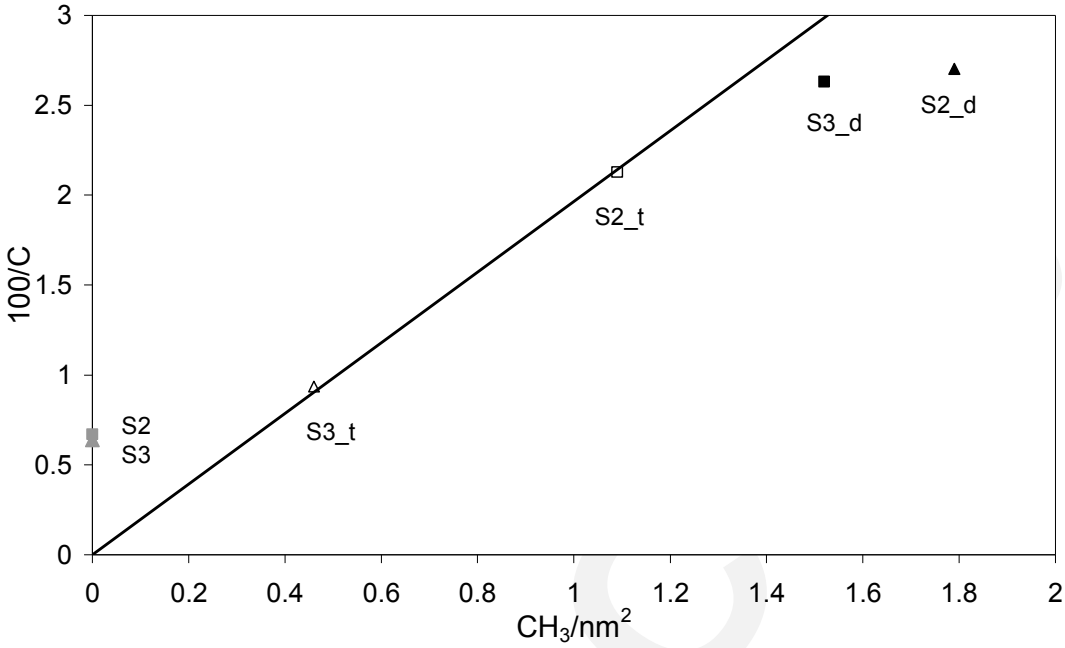
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2
1.5
1
0.5
0
100/C
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
CH3/nm2
S2
S3
S3_t
S2_t
S3_d
S2_d

Figure 7